Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Photochemistry and Photobiology A: Chemistry 176 (2005) 162–171

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Experimental and theoretical studies of the kinetics of the reactions of OH and OD with acetone and acetone-d_6 at low pressure

M.E. Davis [1], W. Drake, D. Vimal, P.S. Stevens *

Environmental Science Research Center, School of Public and Environmental Affairs and Department of Chemistry, Indiana University, 1315 E. 10th Street, Bloomington, IN 47405, USA

Available online 23 September 2005

Abstract

The kinetics of the reactions of OH and OD with acetone and acetone-d_6 were studied from 2–5 Torr and 258–402 K using a discharge flow system with laser induced fluorescence or resonance fluorescence detection of the OH radical. The rate constants at 300 K for the reaction of OH with acetone and acetone-d_6 were $(1.73 \pm 0.06) \times 10^{-13}$ and $(3.36 \pm 0.32) \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}, respectively. The rate constants at 300 K for the reaction of OD with acetone and acetone-d_6 were $(2.87 \pm 0.22) \times 10^{-13}$ and $(3.69 \pm 0.12) \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}, respectively. Above room temperature, the temperature dependence of the rate constants for the OH + acetone and acetone-d_6 display Arrhenius behavior and are described by the equations $k_H(T) = (3.92 \pm 0.81) \times 10^{-12} \exp(-938 \pm 70/T)$ and $k_D(T) = (8.19 \pm 1.45) \times 10^{-12} \exp(-1647 \pm 58/T)$ cm^3 $molecule^{-1}$ s^{-1} for acetone and acetone-d_6, respectively. Measurements of k_H and k_D below room temperature begin to display non-Arrhenius behavior, consistent with previous measurements at higher pressures. Theoretical calculations of the kinetic isotope effect as a function of temperature are in good agreement with the experimental measurements using a hydrogen abstraction mechanism that proceeds through a hydrogen-bonded complex.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Hydroxyl radical; Acetone; Kinetics; Isotope effect; Atmospheric chemistry

1. Introduction

Acetone is an important compound in the troposphere with a source strength of approximately 40–95 Tg yr^{-1}, with concentrations of 0.1 to 1 ppb in the free troposphere [1–3]. With a lifetime of 10–30 days based on photolysis and reaction with the OH radical, acetone can have a significant impact not only on local air quality, but also on global tropospheric ozone concentration and upper tropospheric chemistry [4]. In the upper troposphere, where the concentration of water molecules is low, acetone is also thought to be a major source of the OH radical, in some cases accounting for 50% of the total HO_x concentration [4]. In the lower troposphere, the reaction with the OH radical is the major removal pathway.

The OH + acetone reaction can occur either by the abstraction of a hydrogen atom or by the addition of the OH radical to the carbonyl group (reactions (1) and (2)):

$$CH_3COCH_3 + OH \rightarrow CH_2C(O)CH_3 + H_2O \quad (1)$$

$$CH_3COCH_3 + OH \rightarrow CH_3C(O)OH + CH_3 \quad (2)$$

These radical products undergo subsequent reactions resulting that can lead to the net formation of OH radicals. In order to accurately predict the HO_x formation rate from acetone and the fate of acetone in the troposphere, it is important to know the overall rate constant for the OH + acetone reaction and the branching ratio for reactions (1) and (2).

Previous measurements of the rate constant for the reaction of acetone with the hydroxyl radical using both absolute and relative rate techniques [5–14] have generally showed that the rate constant follows Arrhenius behavior between 240 and 400 K [10,11,13,14]. However, recent measurements have revealed that at upper tropospheric temperatures the rate constant displays non-Arrhenius behavior, becoming independent of temperature below 260 K [10,13].

The non-Arrhenius behavior of the OH + acetone reaction had been hypothesized by Wollenhaupt et al. [10] as a shift in the mechanism from primarily H-abstraction at high tem-

---

* Corresponding author. Tel.: +1 812 855 0732
E-mail address: pstevens@indiana.edu (P.S. Stevens).

[1] Present address: Aeronomy Laboratory, National Oceanic and Atmospheric Administration, 325 Broadway, Boulder, CO 80305, USA.

1010-6030/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2005.08.030

perature (∼90% at 400 K) to 50% each H-abstraction and OH-addition at 280 K, and to primarily OH-addition at lower temperatures (∼90% addition at 210 K) (reactions (1) and (2)). A branching ratio of 0.5 at 298 K had been inferred from experiments conducted by Wollenhaupt and Crowley [11], who measured the production of the methyl radical (CH_3), which is the expected product from the addition mechanism (reaction (2)), while Vasvari et al. [12] measured the 1-methylvinoxy radical ($CH_2C(O)CH_3$) formed from the abstraction mechanism (reaction (1)). Wollenhaupt and Crowley [11] also found evidence that the branching ratio for the addition mechanism decreased with temperature to 0.3 at 233 K.

In contrast, Vandenberk et al. [15] found no significant production of acetic acid from reaction (2), consistent with transition state theory and RRKM —master equation calculations demonstrating that the barrier for OH addition is significantly greater than that for hydrogen abstraction. Tyndall et al. [16] also found no evidence for direct formation of acetic acid from reaction (2). Similar results were reported by Talukdar et al. [17], who measured a yield for the acetonyl radical of (96 ± 11)%, independent of temperature between 237 and 353 K, and found that the yield of acetic acid from the reaction was less than 1%. Turpin et al. [18] also measured the yield of the acetonyl radical (relative to the acetonyl radical yields from the F + acetone and Cl + acetone reactions), suggesting a yield for reaction (1) between 80 and 100% at 298 K. Theoretical studies by Masgrau et al. [19] are also consistent with these results, suggesting that the acetic acid yield is less than 2% and decreases with temperature. Recent measurements by Raff et al. [20] using online mass spectrometry are also consistent with a yield of acetic acid of approximately 3% from the OH + acetone reaction, but measurements of the production CD_3COOH from the OH + acetone-d_6 reaction resulted in a measured yield of approximately 18% at 298 K that increased with decreasing temperature.

Gierczak et al. [13] studied the OH + acetone and OH + acetone-d_6 reactions as well as the ^{18}OH + acetone, the OD + acetone, and the OD + acetone-d_6 reactions as a function of temperature. They found a large primary kinetic isotope effect for the OH + acetone and OH + acetone-d_6 reactions, indicating that the reaction mechanism primarily involves hydrogen abstraction even at low temperatures. Talukdar et al. [17] measured the rate constant for the OH + acetone reaction at pressures of 1–3 Torr as a function of temperature, and found that the rate constant did not exhibit a significant pressure dependence, consistent with a hydrogen abstraction reaction. Farkas et al. [21] also measured the kinetic isotope effect at low pressure, finding value of 5.33 ± 0.41 at 298 K, consistent with measurements at higher pressure.

Based on the large primary kinetic isotope effect measured at low temperatures, Gierczak et al. [13] suggested that the formation of a pre-reactive addition complex in the hydrogen abstraction mechanism could explain the non-Arrhenius behavior rather than a shift in the mechanism from abstraction to addition, similar to that proposed for the OH + HNO_3 reaction [22]. Theoretical calculations of the kinetic isotope effect using variational transition state theory by Yamada et al. [14] using a mechanism similar to that of Gierczak et al. were able to reproduce the observed kinetic isotope effect for wide range of temperatures. However, the theoretical calculations overestimated the observed kinetic isotope effect at temperatures below 250 K, predicting an isotope effect greater than 10 at 200 K. Farkas et al. suggest that such a mechanism might lead to a kinetic isotope effect as high as 10, similar to that observed for the OH reactions with HNO_3 and DNO_3, and that the observed kinetic isotope effect of approximately 5–6 is not inconsistent with a mechanism that involves both addition and abstraction [21]. Unfortunately, there have been fewer measurements of the rate constant for the OH + acetone-d_6 reaction, especially at temperatures below 300 K.

This paper examines the kinetics of the OH + acetone and acetone-d_6 reactions at 2–5 Torr and 258–402 K. In addition, the room temperature rate constants for the OD + acetone and acetone-d_6 reactions were also measured. These are the first measurements of the temperature dependence of the kinetic isotope for this reaction at pressures less than 10 Torr. Results of ab initio calculations of the energetics of the intermediates and transition states for the OH + acetone and OH + acetone-d_6 reactions were used in conjunction with unimolecular rate theory to calculate the kinetic isotope effect as a function of temperature and determine if the observed kinetic isotope effect is consistent with a mechanism for this reaction involving hydrogen abstraction through an intermediate complex.

2. Experimental methods

Experiments were conducted using the discharge-flow (DF) technique using either resonance fluorescence (RF) or laser induced fluorescence (LIF) detection of the OH radicals. The experimental systems are similar to those described previously [23]. The reactor is a jacketed 100 cm long, 25 mm internal diameter Pyrex glass tube to which ports that allow the addition of gases are attached. A movable injector (3 mm o.d.) inserted into the flow-tube is used for the introduction of acetone and acetone-d_6. The injector and all areas of the flow-tube exposed to radicals were coated with halocarbon wax (Halocarbon Corporation) to reduce the loss of radicals on the reactor walls. Bulk flow velocities of 9.4–10.7 m s^{-1} were achieved at 300 K using a Leyland D16B mechanical pump downstream of the detection zone. The reaction temperature was varied by circulating heated silicone oil or liquid nitrogen cooled ethanol through the jacket of the flow-tube. The temperature was monitored using a thermocouple located in the center of the reaction zone. Helium, used for the bulk flow gas, was introduced into the system by a MKS 1179 flow controller. The reactor pressure was measured in the reaction zone by a MKS Baratron capacitance manometer.

OH radicals were produced using the $H + NO_2 \rightarrow OH + NO$ reaction ($k^{II} = 1.3 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}). H atoms were produced from a microwave discharge (Opthos Instruments Inc., model MPG-4) of H_2 in He. NO_2 ($(2–6) \times 10^{13}$ molecules cm^{-3}) was added in excess 2 cm upstream of the radical source to produce OH radicals. OD radicals were produced in a similar fashion using the $D + NO_2 \rightarrow OD + NO$ reaction, producing D atoms from a microwave discharge of D_2 in He.

Download English Version:

https://daneshyari.com/en/article/9605444

Download Persian Version:

https://daneshyari.com/article/9605444

Daneshyari.com